(2)

Naval Research Laboratory
Washington, DC 20375-5000

NRL Memorandum Report 6291

Material Compatibility with Threshold Limit Value Levels of Monomethyl Hydrazine

P. A. TAFFE, S. L. ROSE-PEHRSSON AND J. R. WYATT

Chemical Dynamics and Diagnostics Branch
Chemistry Division

October 26, 1988

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No 0704-0188

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): NRL Memorandum Report 6291	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Naval Research Laboratory; 6b OFFICE SYMBOL (If applicable): Code 6110	7a NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code): Washington, DC 20375-5000	7b ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: National Aeronautics and Space Admin.; 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code): Kennedy Space Center, FL 32899	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Material Compatibility with Threshold Limit Value Levels of Monomethyl Hydrazine

12 PERSONAL AUTHOR(S)
Taffe, P.A., Rose-Pehrsson, S.L. and Wyatt, J.R.

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year Month Day)	15 PAGE COUNT
Final	FROM ____ TO ____	1988 October 26	33

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Threshold limit value (~~TLV~~), Monomethyl hydrazine, Sampling lines, Vapor detection

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Materials were evaluated for potential use as ambient air sample lines for hydrazines. Fluorinated polymers performed the best, metals the worst. Various sample lengths were investigated: increasing the length enhanced the differences between samples, although the ranking of performance remained essentially unchanged. The effects of internal diameter (id) upon transport ability was evaluated by testing samples with ids of 3/16, 1/4, and 3/8 inch. The 3/8 inch id tubing consistently transported a larger percentage of the contaminant. Additional areas examined for their effects on performance were: temperature, humidity, joining of segments, pushing the pulling of the gas stream, and conditioning of the sample tube. The only variable found to have a significant effect on the results was conditioning; indicating that all new tubing should be thoroughly rinsed prior to use as well as periodically between sampling to remove ambient contaminants.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL: Jeffrey R. Wyatt	22b TELEPHONE (Include Area Code): (202) 767-3244; 22c OFFICE SYMBOL: Code 6112

DD Form 1473, JUN 86 Previous editions are obsolete SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

CONTENTS

MATERIAL COMPATIBILITY WITH THRESHOLD LIMIT VALUE LEVELS OF MONOMETHYL HYDRAZINE

INTRODUCTION

The use of hydrazine (Hz), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH), especially as high energy propellants, has increased dramatically in recent years. The space shuttle program requires large amounts of both Hz and MMH. In addition, substantial quantities of hydrazines are used as propellants in Titan ballistic-missiles, satellites, and aircraft auxiliary-power units. With this increased usage, concern has developed over the toxicological properties of the hydrazines.

Studies indicate that exposure to hydrazines may cause damage to the liver, kidneys, and other internal organs and may produce blood abnormalities. Hydrazines not only cause physical damage but also alter the behavior of personnel by significantly decreasing performance capabilities.[1] A recent study cites irreversible damage to the nervous system as a possible consequence of hydrazines exposure.[2] Effects in man can be teratogenic as well as mutagenic. The adverse effects extend to nonmammalian life forms, thereby potentially endangering the environment.

Since the hydrazines are suspected carcinogens, a maximum tolerated toxic level has been set at five parts-per-million (ppm). The American Conference of Governmental Industrial Hygienist (ACGIH) has recommended the threshold limit values (TLV) of Hz, MMH, and UDMH to be 100, 200, and 500 parts-per-billion (ppb), respectively.[1] To protect personnel from overexposure, NASA, the Air Force, and the Department of Defense, require air monitoring for hydrazines in areas where they are handled and/or stored.

For several reasons, it is desirable to monitor a number of these potential exposure sites with one fixed-point analyzer which samples through a network of tubing in which sections may be 200 feet or more in length. With many ambient air contaminants this

---

Manuscript approved July 29, 1988.

method of sampling would pose no addition problems, but due to the reactive nature of hydrazines and their known interaction and decomposition on surfaces, the transport tubing could significantly effect the concentration of MMH to reach the analyzer.

This report describes the results of a materials compatibility study comparing the ability of several commercially available tubings to transport TLV levels of MMH under various conditions. The object of this study was to determine which tubing type(s) optimumly transport hydrazine contaminated air. Table 1 lists the types of tubings tested during the screening test. Variables studied for their effects on performance include: temperature, humidity, length of tubing, internal diameter of tubing, jointing segments verses one continuous piece, pushing and pulling of the gas stream, new tubing with no conditioning or washing, methanol washing of tubing, and the performance of tubing conditioned with ambient air. This study was approached as a survey rather than a statistical analysis due to the time allotted and the number of variables to be investigated.

EXPERIMENTAL

Figure 1 is a schematic of the test apparatus which was constructed of FEP teflon. The air supply was house-compressed air conditioned by passing through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular-sieve scrubber, and finally through a canister containing potassium permangenate coated alumina (PURAFIL) and charcoal. The clean air was rehumidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of relative humidity was achieved by varying both the gas washer head pressure and the ratio of rehumidified to dry air. A mass flow controller passed 4.9 liters per minute of zero grade, humidified air through a chamber where the humidity was measured by a hygrometer. Finally, the air flow was controlled by a solenoid valve system attached to the coil of

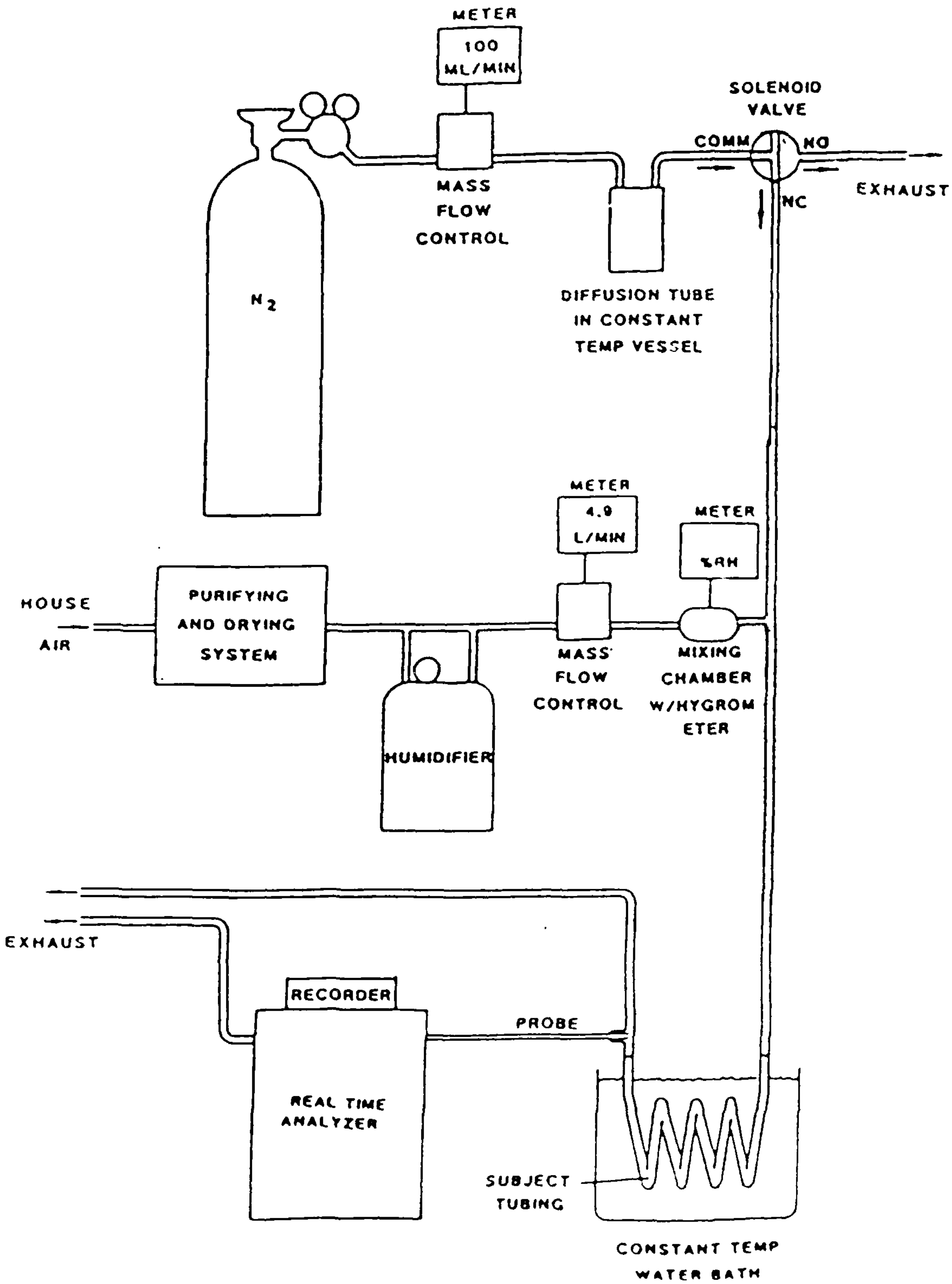

Figure 1. Apparatus for testing of material compatibility.

tubing to be tested. Control of the sample tubing temperature was achieved by placing the tubing into a water bath, where the water was circulated from an exterior constant temperature bath.

Monomethylhydrazine vapor was generated from a diffusion tube held at 32°C. The MMH was swept from the diffusion tube with 100 ml/min dry nitrogen to the above mentioned teflon solenoid valve system which normally vents the MMH. When activated, the solenoid valve controls mixing of MMH with the clean air at a point just ahead of the sample tubing inlet. This is the technique used to deliver the TLV level, 200ppb, of MMH. Impinger samples were collected at this location to verify the MMH concentration. They were analyzed by a coulometric titration with bromide and amperometric endpoint detection. The coulometric method is the NRL/White Sands modification of reference 3, in which we miniaturized the system to improve sensitivity. This concentration measurement was performed before and after each tubing challenge test.

Real-time monitoring of ppb levels of MMH was accomplished using one of two instruments. The majority of tests utilized the TECO analyzer, which is a chemiluminescence-based breadboard instrument developed by Thermo Electron Corporation (now Thermedics, Inc.). The response time of this instrument is a few seconds which is considered to be real-time for our purpose. The results used for comparison were normalized to the full scale deflection (FSD) of the instrument, which was established during the concentration verification procedure, before and after each test. During phase 7 numerous problems were encountered with the TECO instrument and it was replaced with an MDA Scientific Inc., Model 7100 instrument, for real-time monitoring. The MDA 7100 is a commercially available paper tape instrument which measures the color change that develops upon exposure to MMH. The intensity of the color is proportional to the concentration. The color is measured and the concentration is printed every 2 minutes. This technique has few interferences and worked well in these studies.

A typical tubing MMH challenge experiment consisted of three steps. First, the contaminated air stream was monitored with the TECO analyzer through a two inch FEP teflon tube and the FSD was established and recorded. Simultaneously the MMH concentration was verified by coulometric analysis. These values were later used to calculate the amount of MMH transported by a coil of sample tubing in comparison to the amount detected without the coil. Next, the solenoid valve controlling the MMH contaminant was deactivated and the MMH was exhausted to the hood. When the concentration of MMH dropped below detectable limits (about 10 ppb) the subject tubing was connected to the test system and placed in the controlled-temperature water bath. The tubing was allowed to equilibrate by flowing humidified clean air through it for approximately 20 minutes while the TECO analyzer sampled gas from the outlet end of the subject tubing to establish a baseline. Finally, the solenoid valve was activated, providing TLV challenge level of MMH at the subject tube inlet. The outlet of the tubing was monitored.

An example of the data is shown in Figure 2. This data was used to determine the times required to reach 50, 75, 90, and 100 percent of the challenge MMH concentration. The first indication and the time to 50 percent were comparable. When 100 percent transport was not achieved, the maximum percentage of MMH reached and the time required to reach that value was recorded.

At the end of a test, the tubing was rinsed with methanol and dried with compressed breathing air. Cleaning the tubing material between tests had virtually no effect on the results of subsequent tests. Initial washing of new tubing was found to improve the transport performance of some tubings. We postulate that the methanol removes plasticizers or other formulation ingredients of the tubing which may impede transport. Solvents which are ketones, such as acetone, were not used as they react

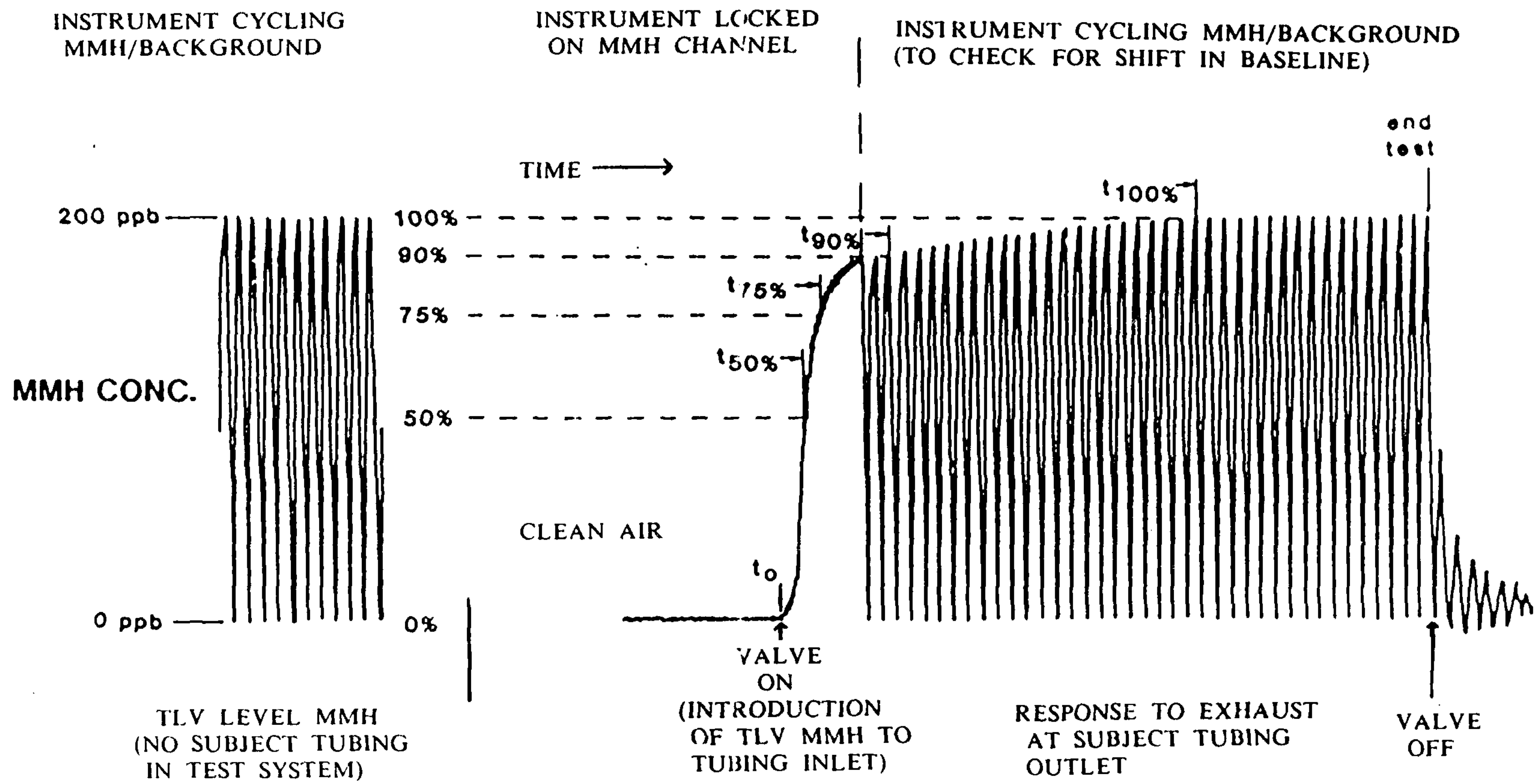

Figure 2. An example of the instrument response to MMH through a coil of tubing.

with hydrazines. Variations and additions to the experimental set-up and design are discussed where applicable in the next section.

EXPERIMENTAL SET-UP AND RESULTS

Phase 1 - Preliminary Screening

A preliminary screening procedure was used in an effort to eliminate the candidates with poor performance. Eight foot lengths of the tubings listed in Table 1 were tested at 21 degrees Celsius and 45 percent relative humidity for a period of 20 minutes. The results are presented in Table 2, and graphically compared in Figure 3. While all metal tubing performed poorly, nearly all other polymeric tubing performed equally in the screening tests. Figure 4 compares all of the metal tubes tested and Figure 5 compares several of the plastic tubes tested. The metals reduced the final equilibrium transport concentration of MMH to 50% or less of the challenge concentration. Tygon and teflon PFA were unable to transport 100% of the MMH. Based upon the results of this preliminary screen, the metals were eliminated from further testing. Materials which did not possess the desired flexibility, such as acrylic and tenite, were also dropped from the evaluation.

Phase 2 - Temperature and Humidity Effects

The selection of candidate tubings for additional testing at lengths of up to 75 feet was based on (1) known or assumed compatibility with hydrazines, (2) cost, (3) flexibility, and (4) resistance to heat. For the second phase of testing, temperatures of 8, 21, and 40 degrees Celsius and relative humidities of 20, 45, and 65 were selected to mimic, as closely as possible, the extremes of expected field conditions. All combinations of temperature and humidity were achieved except 40 C and 65% relative humidity, which was beyond the capability of the humidifying system. Tubing in 75 foot lengths was tested for 40 minutes, lesser lengths for 30 minutes. In some cases, tubings of the same

Table 1. Tubings Evaluated in the Screening Test

Tubing Material	Reference	Supplier	Manufacturer (when available)
Acrylic	ACRY	Read	Thermoplastic Processes, Inc.
Aluminum	ALUM	NRL	
Bev-A-Line IV	BEV	Read	Thermoplastic Scientifics
Brass	BRASS	NRL	
Copper	COPPER	NRL	
Nylon	NYLON	Read	Polymer Corporation
Polycarbonate	PCAR	Read	Thermoplastic Processes, Inc
Polyethylene	POLYETH	NRL	
Polyethylene, High Density	HDPE	NRL	
	"	Read	Hudson Extrusions, Inc.
Polyethylene, Low Density	LDPE	Read	"
Polypropylene	POLYP	Read	"
Rubber	RUBBER	NRL	
Steel	STEEL	NRL	
Teflon FEP	FEP	Read	Atlantic Tubing Company
	"	Norton	Norton
	"	Cole	Zeus
Teflon PFA	PFA	Norton	Norton
Teflon TFE	TFE	Read	Atlantic Tubing Company
	"	Norton	Norton
Tenite	TENITE	Read	Thermoplastic Processes, Inc.
Tygon	TYGON	NRL	

Cole: Cole-Parmer Scientific
NRL: Naval Research Laboratory Supply Store
Norton: Norton Company
Read: Read Plastics

Table 2. Results from Preliminary Screen.

TUBING	LENGTH (FEET)	SOURCE	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENTS
FEP	8	COLE	.75	1.5	2.5	6	100	6	
FEP	8	NORTON	1.25	2.5	9		97	11	
FEP	8	READ	1.5	2	3.5	9	100	9	
PFA	8	NORTON	2.5	3	5		94	9	
TFE	8	NORTON	.75	1	2	6	100	6	
BEV	8	READ	.75	1	2	4	100	4	
TYGON	8	NRL	1	1.5	5		92	6.5	bath cut off during test
FEP	8	COLE	1	2	6		95	12	
FEP	8	COLE	.75	1	2.5	10	100	10	
PFA	8	NORTON	1.25	2	10		94	9	
TFE	8	NORTON	1	1.5	2.5	14	100	14	
TFE	8	READ	1	2	4	11	100	11	
TYGON	8	NRL	1	2	4		95	10	
TYGON	8	NRL	.75	3	4.5		92	8	
POLYETH	8	NRL	1	1.25	2	13	100	13	1/4" internal diameter
POLYETH	8	NRL	1.5	2	4		95	6	1/8" internal diameter
HDPE	8	READ	1.25	2	5	12	100	12	
LDPE	8	READ	1	1.5	3.75	12	100	12	
POLYP	8	READ	1	1.5	2.75	13	100	13	
PCAR	8	READ	2	2.5	4	13	100	13	
POLYETH	8	NRL	1	1.5	2	16	100	16	1/4" internal diameter
POLYETH	8	NRL	1	1.75	3.75		95	13	1/4" internal diameter
POLYETH	8	NRL	1	1.5	4		95	6	1/8" internal diameter
COPPER	8	NRL					7.5	6	
COPPER	8	NRL					7.5	6	
COPPER	8	NRL					5.3	5	
STEEL	8	NRL	17				50	17	
STEEL	8	NRL					45	26	
STEEL	8	NRL					42	18	
STEEL	8	NRL					47	20	
ALUM	8	NRL					15.8	5	
ALUM	4	NRL	13				53	13	
BRASS	8	NRL					6.3	6	
RUBBER	7	NRL	1.25	3.5	9		90	9	
NYLON	8	READ	1.25	2	3.5	8	100	8	
ACRY	6	READ	1.5	2.25	5	12	100	12	
TENITE	6	READ	9	20			75	20	small crack in tubing
BEV	8	READ	.75	1.5	3	8	100	8	
POLYP	8	READ	1	1.75	4.25	8			

Conditions: 20 C, 45% RH, pushing 200 ppb MMH air stream at 5 l/min. All tubing tested for 20 minutes. Internal diameter of tubing was 3/16" unless otherwise noted.

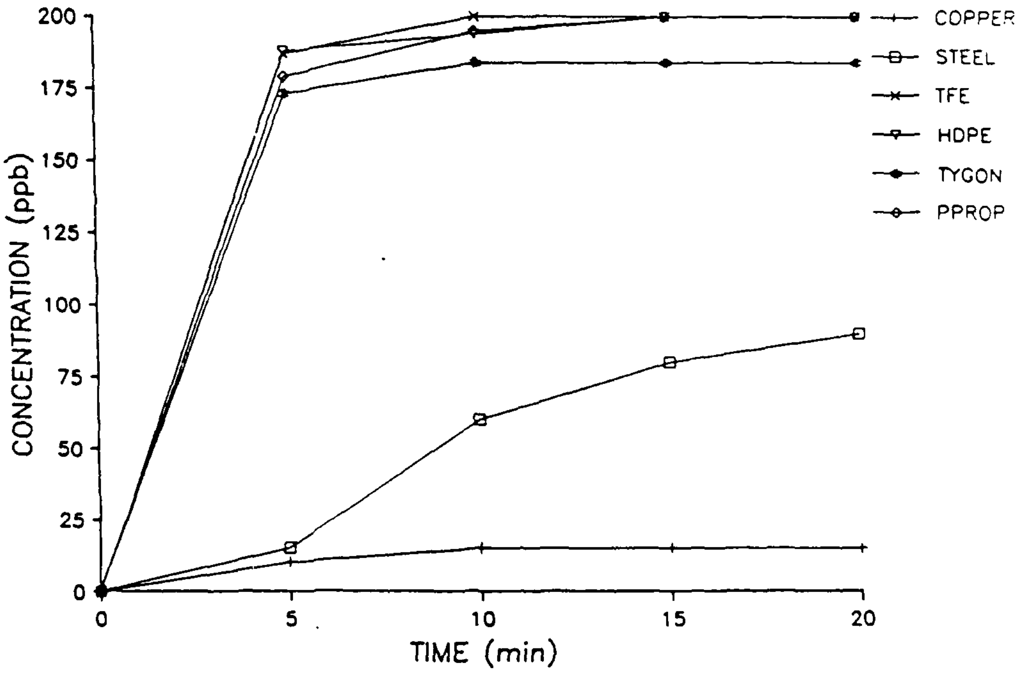

Figure 3. The amount of 200 ppb monomethylhydrazine transported down 8 feet of several different tubes under moderate conditions (21°C and 45% RH).

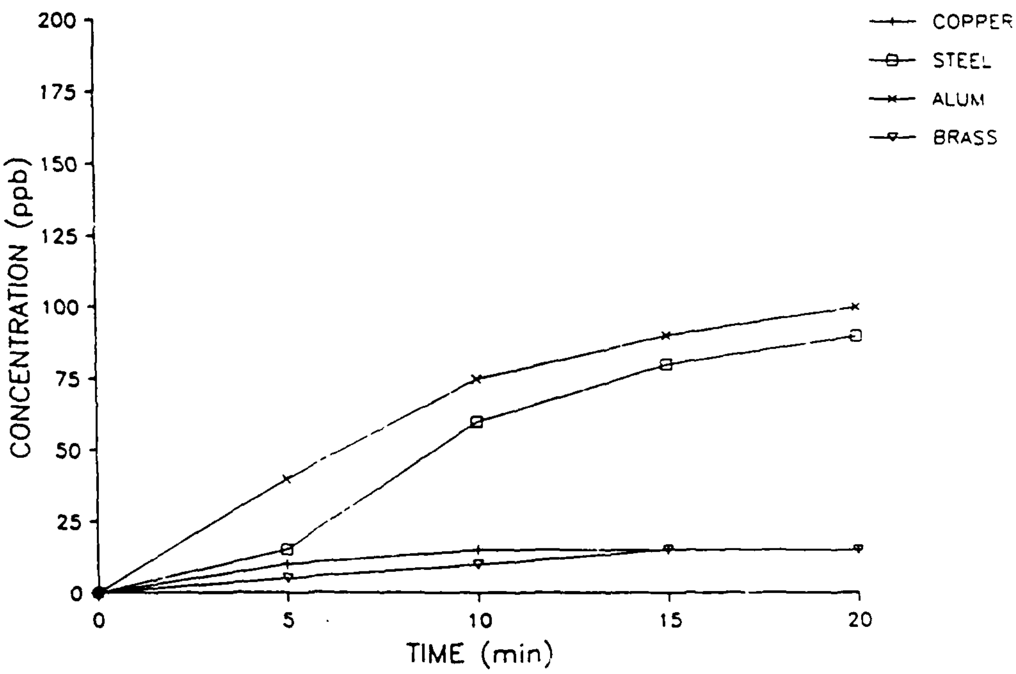

Figure 4. The ability of 8 feet of metal tubing to transport 200 ppb of monomethylhydrazine under moderate conditions (21°C and 45% RH).

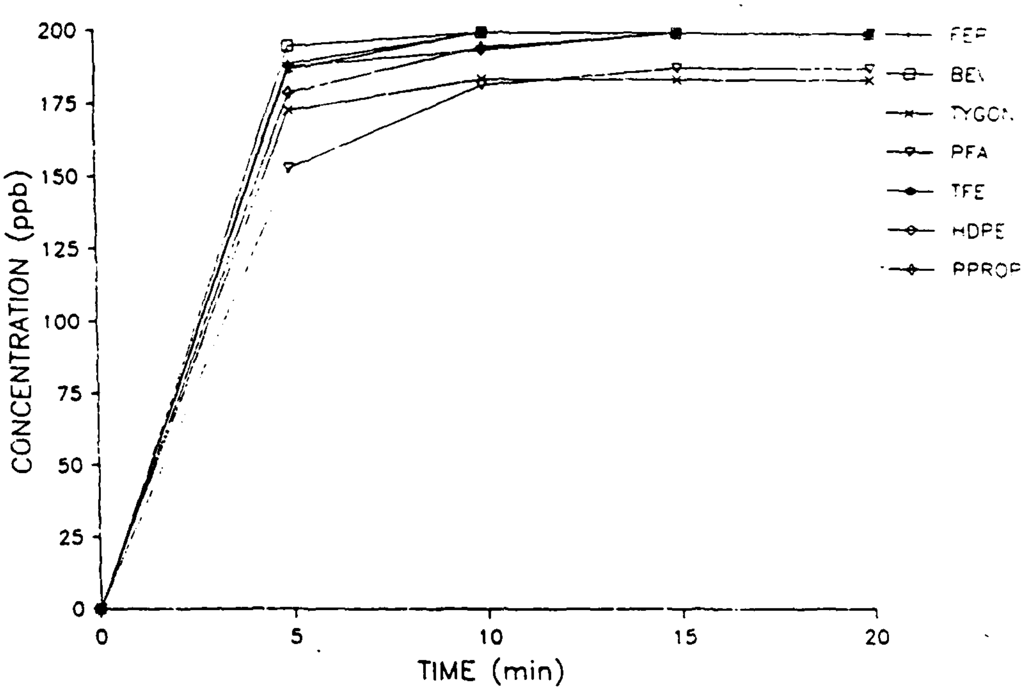

Figure 5. The amount of 200 ppb monomethylhydrazine transported by 8 feet of several different plastic tubes under moderate conditons (21°C 45% RH).

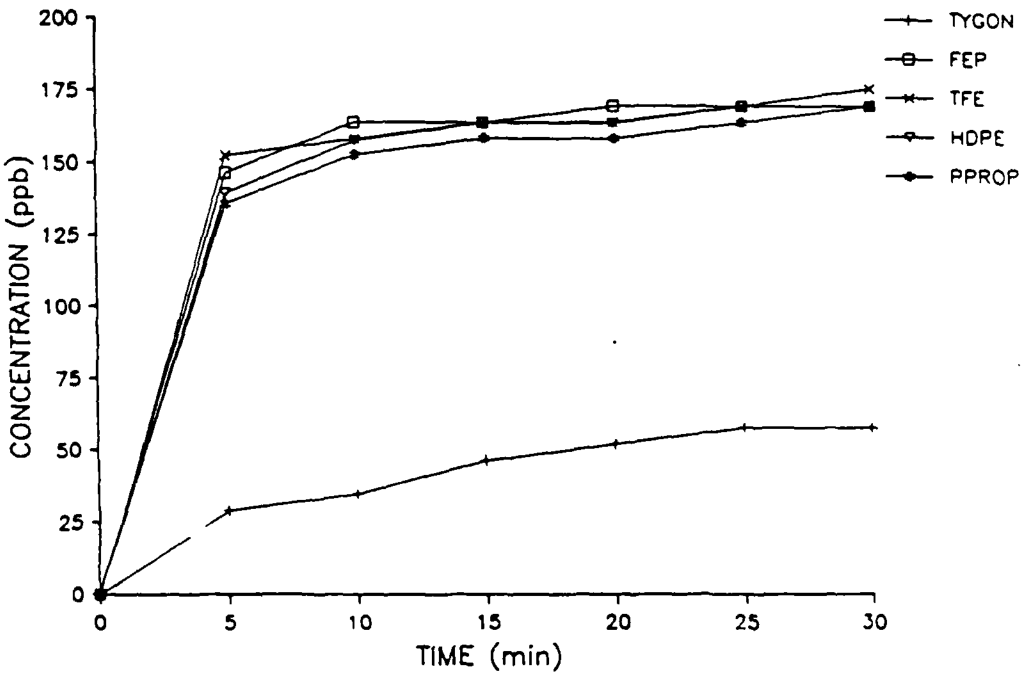

Figure 6. The amount of 200 ppb monothylhydrazine transported by 75 feet of several tubes under moderate conditions (21°C and 45% RH).

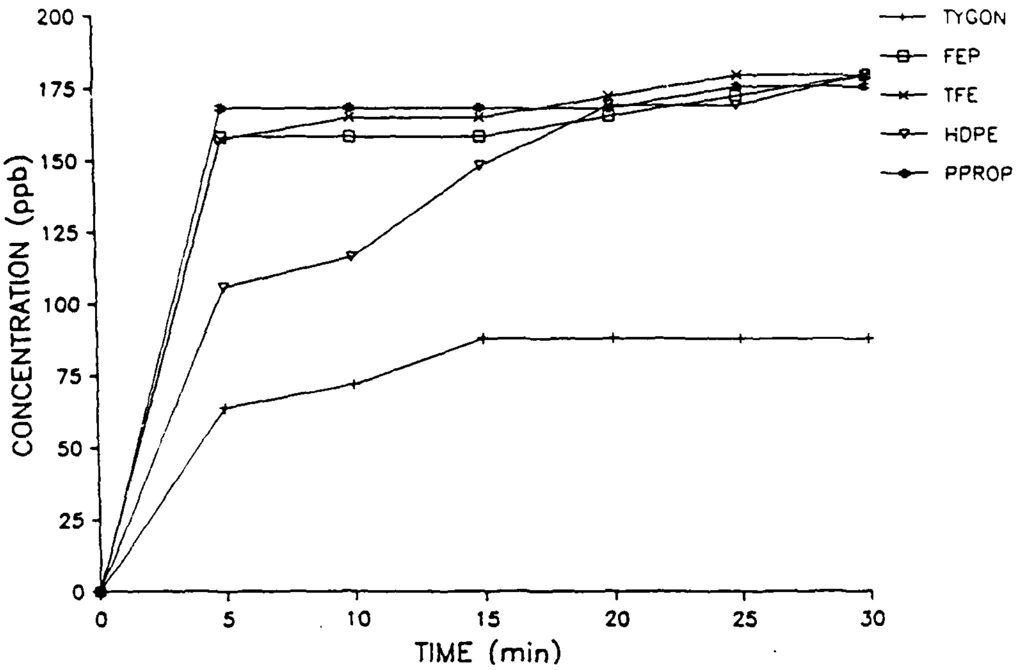

Figure 7. An example of some of the results for transporting 200 ppb monomethylhydrazine at low temperature and high humidity (8°C and 65% RH) through 75 feet of tubing.

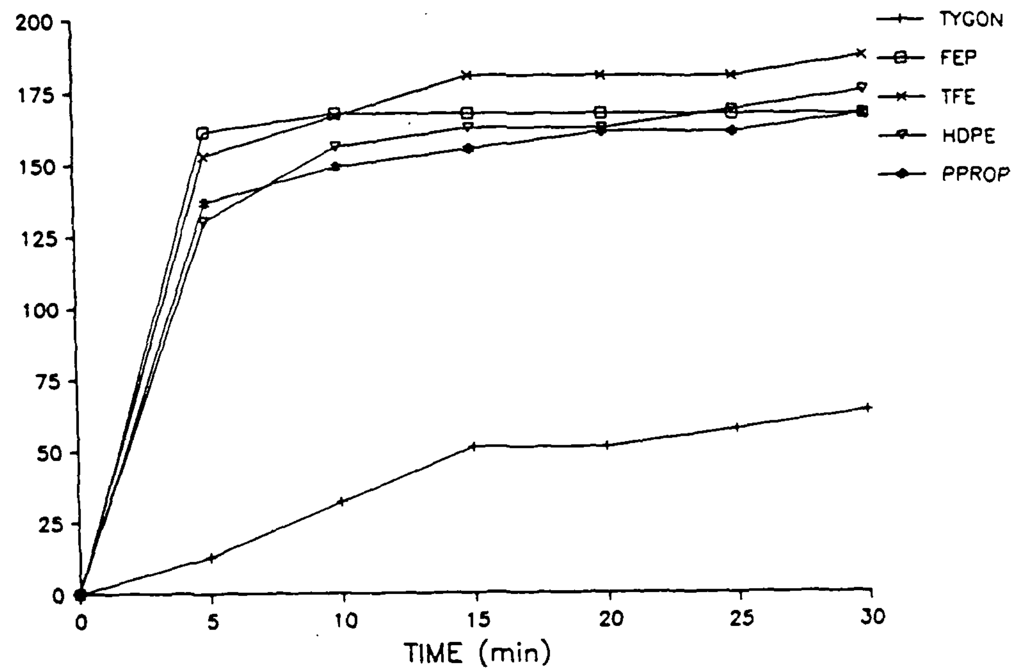

Figure 8. An example of some of the results for transporting 200 ppb monomethylhydrazine at high temperature and low humidity (40°C and 20% RH) through 75 feet of tubing.

type, but from different manufacturers or suppliers, were tested and compared. This was done as a result of data obtained from other test programs at Thermoelectron Corporation and Aerospace Corporation indicating possible wide performance variations based solely upon the source of the tubing. Figures 6, 7 and 8 compare 75 foot lengths of tygon, teflon FEP and TFE, high density polyethylene (HDPE), and polypropylene tubing for three of the conditions tested. Consistently Tygon gave the poorest performance while the other materials were comparable. None of the materials achieved 100% transport of the MMH over 75 feet in a 40 minute challenge. Varying the temperature and relative humidity had little effect on ability of the tubing samples to transport MMH. The relative time required and the magnitude of MMH transported was consistent for all tests. The data are presented in Table 3.

Phase 3 - Effects of Internal Diameter of the Tubing

For selected materials the effect of tubing internal diameter (id) upon transport efficiency of MMH was investigated. Id's of 3/16", 1/4", and 3/8" were evaluated when available. The materials tested and data collected are presented in Table 4. Like materials were purchased from the same supplier in an effort to control potential variables. Maintaining a constant wall thickness between tubing samples was not possible. The assumption was made that this factor would not interfere with the tubing ability to transport the challenge gas, it did however influence the ease of handling. Note the dead volume of 100 feet of 3/16", 1/4", and 3/8" id tubing is 0.53, 0.95, and 2.14 liters respectively. These dead volumes would account for hold ups in transport times of 6, 11, and 26 seconds respectively. Since the results obtained in phase 2 revealed little or no effect from variations in the temperature and relative humidity (RH), one set of nominal conditions was chosen for this series of experiments, 21 C and 20% RH.

Table 3 (a). Tests Involving a 20% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENT
21 C AND 20% RH										
TYGON	75	NRL	40 MIN					44	29	1/8" ID
FEP	75	READ	"	1.5	3	20		91	22	
FEP	75	COLE	"	1	2.5	10		94	24	
TFE	75	READ	"	2	4	16		97	24	
NYLON	75	READ	"	1	2.5	6		97	20	
POLYETH	75	NRL	"	1	2	10	14	100	14	1/4" ID
LDPE	75	READ	"	1.5	5			88	21	
HDPE	75	READ	"	1.75	4			88	17	
POLYP	75	READ	"	1.5	4.5			86	18	
FEP	17	NORTON	30 MIN	1	2.5	6		97	14	
TFE	16	NORTON	"	1	2	5	14	100	14	
PFA	16.5	NORTON	"	1.25	2.25	7		97	15	
BEV	47	READ	"	1	2	4		97	23	1/8" ID
8 C AND 20% RH										
TYGON	75	NRL	40 MIN					39	26	1/8" ID
FEPO	75	READ	"	1.25	3	8		94	14	
FEP	75	COLE	"	.75	1.25	7		94	10	
TFE	75	READ	"	1.5	3	18		90	18	
NYLON	75	READ	"	1	2	10		97	23	
POLYETH	75	NRL	"	1	2	9		94	27	1/4" ID
LDPE	75	READ	"	1.25	3.5			88	21	
HDPE	75	READ	"	1	2.75	19		90	19	
POLYP	75	READ	"	1.5	3	17		91	20	
FEP	17	NORTON	30 MIN	1	2	8		94	12	
TFE	16	NORTON	"	.75	1.5	3	17	100	17	
PFA	16.5	NORTON	"	1	2	9		94	16	
BEV	47	READ	"	.75	1.75	3.5		94	12	1/8" ID
40 C AND 20% RH										
TYGON	75	NRL	40 MIN					32	28	1/8" ID
FEP	75	READ	"	2	3.75			84	5	
FEP	75	COLE	"	1.5	2.5	11		90	11	
TFE	75	READ	"	2	3.5	16		94	24	
NYLON	75	READ	"	2	2.5	25		90	25	
POLYETH	75	NRL	"	2	4.5	21		90	21	1/4" ID
LDPE	75	READ	"	2	4			81	17	
HDPE	75	READ	"	2	5			88	15	
POLYP	75	READ	"	2.75	7			84	20	
FEP	17	NORTON	30 MIN	1.5	2.5	6		94	19	
TFE	16	NORTON	"	1.25	2.25	4		94	12	
PFA	16.5	NORTON	"	1.5	2.75	11		91	17	
BEV	47	READ	"	1.5	2.5	4.5		94	12	1/8" ID

Internal diameter of 3/16" was used unless otherwise noted.

Table 3 (b). Tests Involving a 45% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENT
21 C AND 45% RH										
TYGON	75	NRL	40 MIN					29	20	1/8" ID
FEP	75	READ	"	2.5	4			85	9	
FEP	75	COLE	"	2	4.5			85	15	
TFE	75	READ	"	2	3.5			88	17	
NYLON	75	READ	"	2.25	4			79	10	
POLYETH	75	NRL	"	2	3.5			88	14	1/4" ID
LDPE	75	READ	"	2.5	6			85	14	
HDPE	75	READ	"	2	6			85	13	
POLYP	75	READ	"	1.25	2.5			85	12	
FEP	17	NORTON	30 MIN	1.5	2.5	7		97	18	
TFE	16	NORTON	"	1	1.25	2	14	100	14	
PFA	16.5	NORTON	"	4	5			88	18	
BEV	47	READ	"	1.25	2	3	11	100	11	1/8" ID
8 C AND 45% RH										
TYGON	75	NRL	40 MIN					39	26	1/8" ID
FEP	75	READ	"	1.5	2.5	18		94	16	
FEP	75	COLE	"	1.75	4.5			84	12	
TFE	75	READ	"	2.25	5	20		90	20	
NYLON	75	READ	"	2.75	9			84	15	
POLYETH	75	NRL	"	1.25	3	11		94	16	1/4" ID
LDPE	75	READ	"	1.5	2			88	14	
HDPE	75	READ	"	.75	1.5			84	9	
POLYP	75	READ	"	2	9			81	15	
FEP	17	NORTON	30 MIN	1	2	5	21	100	21	
TFE	16	NORTON	"	1	2	4	11	100	11	
PFA	16.5	NORTON	"	1.75	3	12	.	97	22	
BEV	47	READ	"	1	2.5	7		94	16	1/8" ID
40 C AND 45% RH										
TYGON	75	NRL	40 MIN					26	18	1/8" ID
FEP	75	READ	"	2.5	4	11		94	18	
FEP	75	COLE	"	2	3.5	10		97	24	
TFE	75	READ	"	2.5	5	17		90	17	
NYLON	75	READ	"	2	4	18		90	18	
POLYETH	75	NRL	"	1.25	2.25	15		94	24	1/4" ID
LDPE	75	READ	"	2	7			84	21	
HDPE	75	READ	"	2.5	7			84	18	
POLYP	75	READ	"	2.5	9			84	15	
FEP	17	NORTON	30 MIN	2	3	5	13	100	13	
TFE	16	NORTON	"	1.5	2.5	4.5	16	100	16	
PFA	16.5	NORTON	"	1.75	2.25	3		94	15	
BEV	47	READ	"	1.5	2.5	7		94	12	1/8" ID

Internal diameter of 3/16" used unless otherwise noted.

Table 3 (c). Tests Involving a 65% Relative Humidity Atmosphere

TUBING	LENGTH (FEET)	SUPPLIER	TEST DURATION	50% (MIN)	75% (MIN)	90% (MIN)	100% (MIN)	MAX %	MIN TO MAX. %	COMMENT
21 C AND 65% RH										
TYGON	75	READ	40 MIN					43	27	1/8" ID
FEP	75	READ	"	1.75	3	10		93	14	
FEP	75	COLE	"	2.5	4.5	17		93	25	
TFE	75	READ	"	2.75	4	17		93	22	
NYLON	75	READ	"	8				70	21	
POLYETH	75	NRL	"	2	3.5	13		90	13	1/4" ID
LDPE	75	READ	"	4.75	23			75	23	
HDPE	75	READ	"	1.75	5			83	10	
POLYP	75	READ	"	2	5			83	15	
FEP	17	NORTON	30 MIN	1.75	3	5	16	100	16	
TFE	16	NORTON	"	1.5	2.5	4	13	100	13	
PFA	16.5	NORTON	"	2	3	7	16	100	16	
BEV	47	READ	"	1.5	2.25	4	20	100	20	1/8" ID
8 C AND 65% RH										
TYGON	75	NRL	40 MIN					44	19	1/8" ID
FEP	75	READ	"	2	4	24		90	24	
FEP	75	COLE	"	1.5	2.5	6		90	6	
TFE	75	READ	"	1.5	2.75	17		90	17	
NYLON	75	READ	"	10				65	25	
POLYETH	75	NRL	"	1	1.75	7		96	22	1/4"ID
LDPE	75	READ	"	1.25	2.5	13		90	13	
HDPE	75	READ	"	1	2	17		90	17	
POLYP	75	READ	"	1.5	2			88	22	
FEP	75	NORTON	"	.75	1.25	1.75	9	100	9	
TFE	16	NORTON	30 MIN	1	1.5	2	12	100	12	
PFA	16.5	NORTON	"	1	1.5	2		96	9	
BEV	47	READ	"	1.25	1.75	2.5		96	15	1/8" ID

At 40 C the maximum relative humidity attainable with our set-up was 45%.

Internal diameter of 3/16" used unless otherwise noted.

Table 4. Phase 3: Effects of Internal Diameter on Transport

Tubing Material	Length (Feet)	Internal Diameter	50% (Min)	75% (Min)	90% (Min)	Max Percent	Min to Max %
BEV-A-LINE	75	3/16"	1	1.75	14	91.9	17
BEV-A-LINE	75	3/8"	1	2	3	100	32
FEP	75	1/4"	3	5.5	--	89	16
FEP	75	3/8"	1	3	12	93.5	18
HDPE	75	3/16"	1	2	--	84	18
HDPE	75	1/4"	1	2	7.5	90	7.5
HDPE	75	3/8"	1	2	6	96.8	50
PFA	75	3/16"	2.5	6	--	79	9
PFA	75	1/4"	3	7	36	90	36
PFA	75	3/8"	2.5	12	--	81.4	34
POLYPROP	75	3/16"	1	1.5	--	88	5
POLYPROP	75	1/4"	1	2	5	93.2	34.5
POLYPROP	75	3/8"	1	2	5.5	96.7	25
TFE	75	3/16"	1.25	2.5	12	90	12
TFE	75	1/4"	2.25	5	82	90	82
TFE	75	3/8"	3.5	8	21	95	48

Conditions: 21 C, 20% RH, pushing 200 ppb MMH air stream at 5 l/min

The data indicates interactions more complex than the expected direct relationship to surface area. The changes in the id did not measurably affect the time required to transport 50% of the MMH for Bev-a-line IV, HDPE, PFA, or polypropylene. For 75% of the MMH to be transported, the 3/8" id PFA took twice the transport time as the 3/16" id and the 1/4" id of the same material, the FEP gave the opposite results where the 3/8" id took approximately one half the time. The transport time of MMH through TFE increased with diameter. By the 90% transport point only, the HDPE (1/4" and 3/8" ids) and polypropylene (1/4" and 3/8" ids) showed no significant differences between the ids. The 3/8" id Bev-a-line IV reached 90% transport in nearly one fifth the time required for 3/16" id. The FEP tubing with 3/8" id reached 90% transport in twelve minutes, the 1/4" id never transported 90%.

Generally the 3/8" id tubings transported closer to 100% of the MMH. The basic ranking of material efficiency was not altered by varying the id. For the remaining experiments, 1/4 inch id tubing was selected because it was easier to work with and obtain. The 3/8 inch id tubings had two major problems; the thin walled samples had a tendency to crimp, and the thicker walls did not exhibit the desired flexibility.

Phase 4 - Effects of Teflon Jointing of Tubing Segments

To achieve the desired lengths of tubing for testing, it was sometimes necessary to connect multiple segments. This was done with molded teflon Swagelok fittings. To investigate the effects these fittings would have on results, a test was conducted in which a 75 foot continuous piece of high density polyethylene (HDPE) was tested, cut into segments, connected with fittings, and re-evaluated. The results showed no significant effects that can be attributed to the jointing. The tubing was rinsed with methanol between each test to eliminate the potential conditioning which may have occurred from the previous exposure. The data from this experiment is given in Table 5 and depicted in Figure 9.

Table 5. Effects from Teflon Jointing of HDPE Tubing Segment

Length (Feet)	ID (Inch)	Segment Length	50% (Min)	75% (Min)	90% (Min)	Max %	Min to Max
75	1/4	75'	1	2	7.5	90	7.5
75	1/4	75'	1	2	7	90	7
75	1/4	25'+50'	1	1.75	5	94	18
75	1/4	25'+25'+25'	1.25	2.5	21	90	21

Conditions: 21 C, 20% RH, pushing 200 ppb MMH air stream at 5 l/min

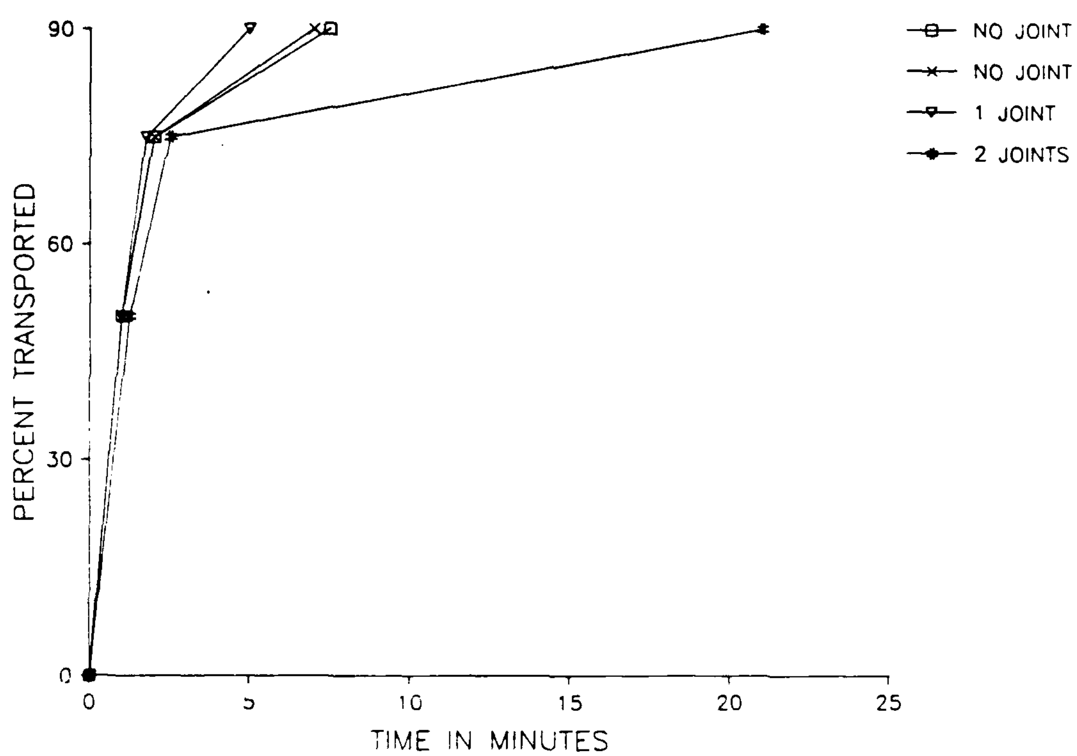

Figure 9. The ability of the same 75 feet of HDPE to transport 200 ppb MMH when used as one continuous piece or as jointed segments.

Phase 5 -Effects of Tubing Length on Transport Efficiency

A larger than expected increase in transport time was observed for lengths of 200 feet. The relationship of length to efficiency was investigated using a 200 foot sample of polyethylene. It was tested at full length and following a series of 20 foot reductions. The data collected is presented in Table 6 and Figures 10 and 11.

A higher percentage of MMH was transported through short tubing samples. Figure 11 graphically represents the time required to transport 75% of the MMH verses length of tubing. At the same time, lengths between 75 and 180 feet require comparable time to reach 50% transport. In addition, for the material tested, lengths under 120 feet were the only samples to achieve 90% or greater transport of the MMH assault gas.

Phase 6 - Introduction of MMH Stream, Pushing vs Pulling

Most air monitoring instruments pull the air through the tubing, therefore the effect of pulling the stream rather than pushing was examined. The set-up used for previous tests involved the pushing of the contaminated air stream through the tubing using the equipment as described earlier, (fig. 1). Slight modifications of the design were made for this phase of testing. During pulling experiments an additional tee was placed between the air source outlet and the tubing inlet. A personnel sampling pump, pulling two liters per minute, was attached to one port on a tee at the exit end of the sample tubing. An impinger containing 0.1 M sulfuric acid was placed in line just prior to the pump to remove the MMH. The third port of this tee was used to connect the TECO analyzer, which pulled an additional 1 liter per minute. These accounted for a total flow through the tubing of 3 liters per minute. The set-up is depicted in figure 12.

In our experiment, we found no significant difference in the final measured concentration based on the method the gas is transported. The data collected is located in Table 7. The flow rates through the tubing were slower for pulling verses pushing

Table 6. Effects of Tubing Length upon Transport Using 1/4" Polyethylene

Length (Feet)	50% (Min)	75% (Min)	90% (Min)	Maximum Percent	Minutes to Max
* 200	27	262	--	81	528
* 200	36	162	--	82	684
200	10	54	--	86	474
180	3	11	--	88	84
160	3.5	28.5	--	89	300
140	3	9	--	89	60
120	4	12	136	90	136
100	3	11	36	94	261
75	2.5	10	37	90	37
8	1	1.25	2	100	13

Conditions: 19 C, 45% Relative Humidity, Pushing 200 PPB MMH

* Tested prior to rinsing with methanol

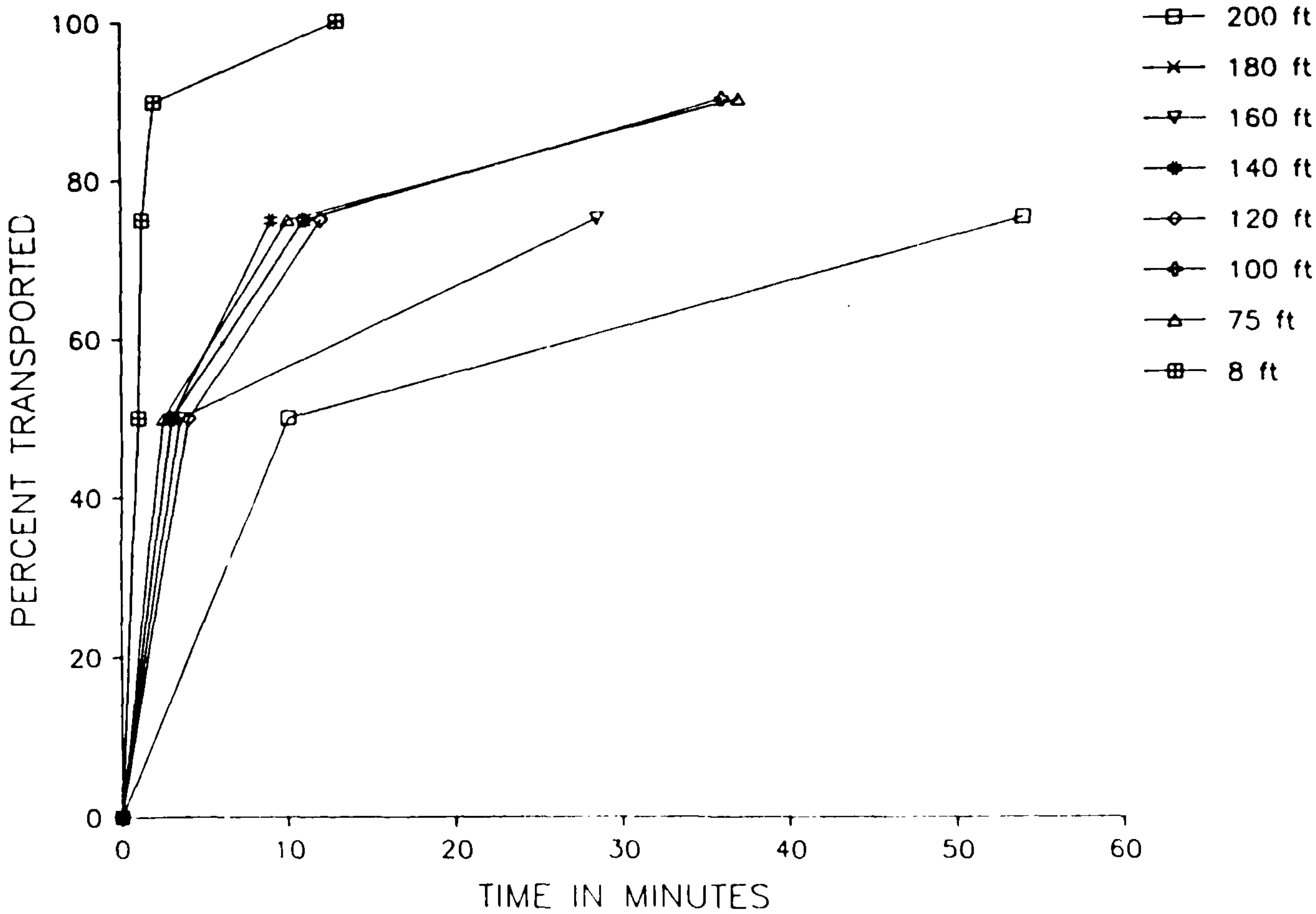

Figure 10. The effect of sample line length upon transport efficiency.

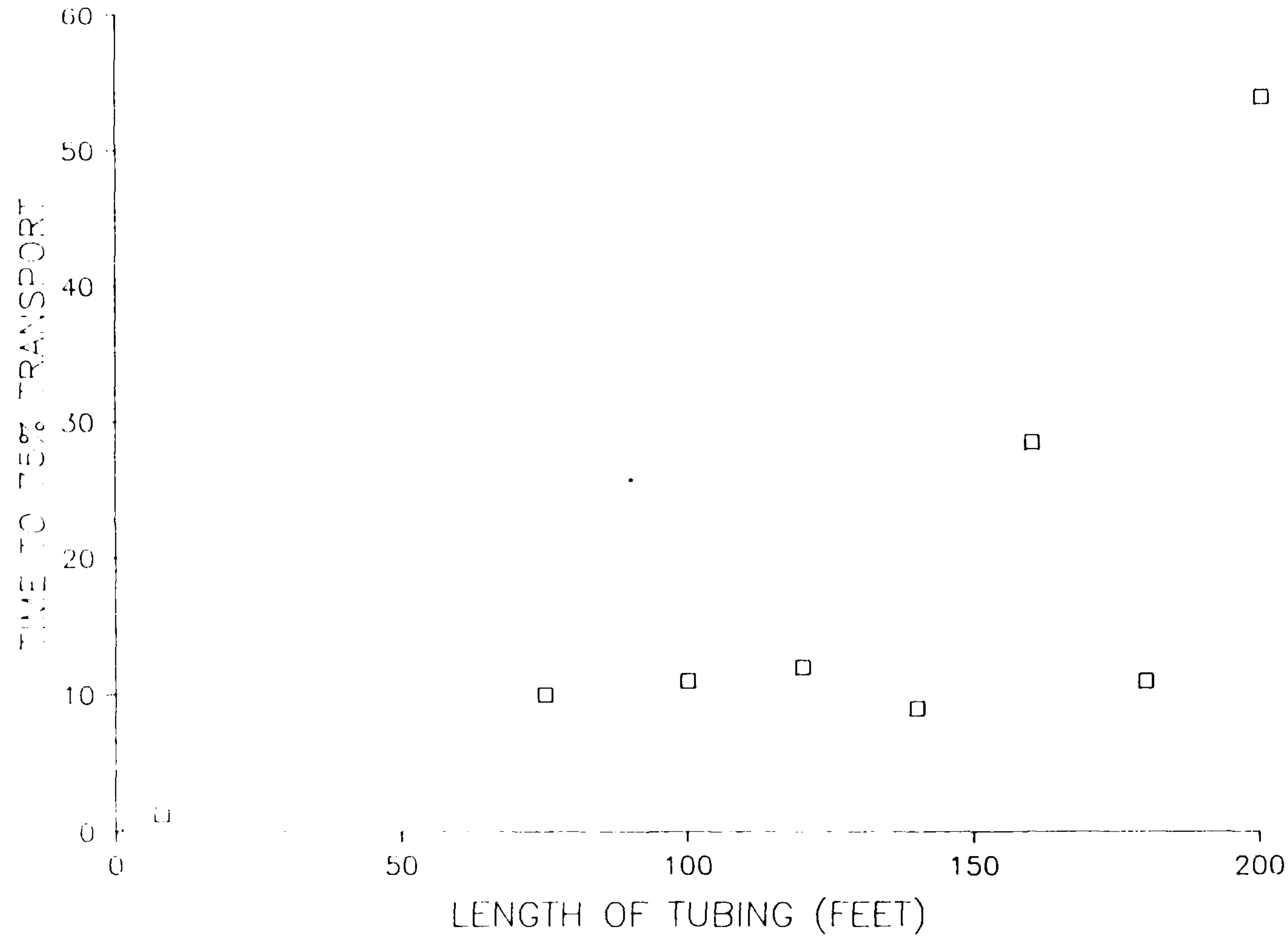

Figure 11. The effect of sample line length upon the time required to transport 75% of MMH (200ppb).

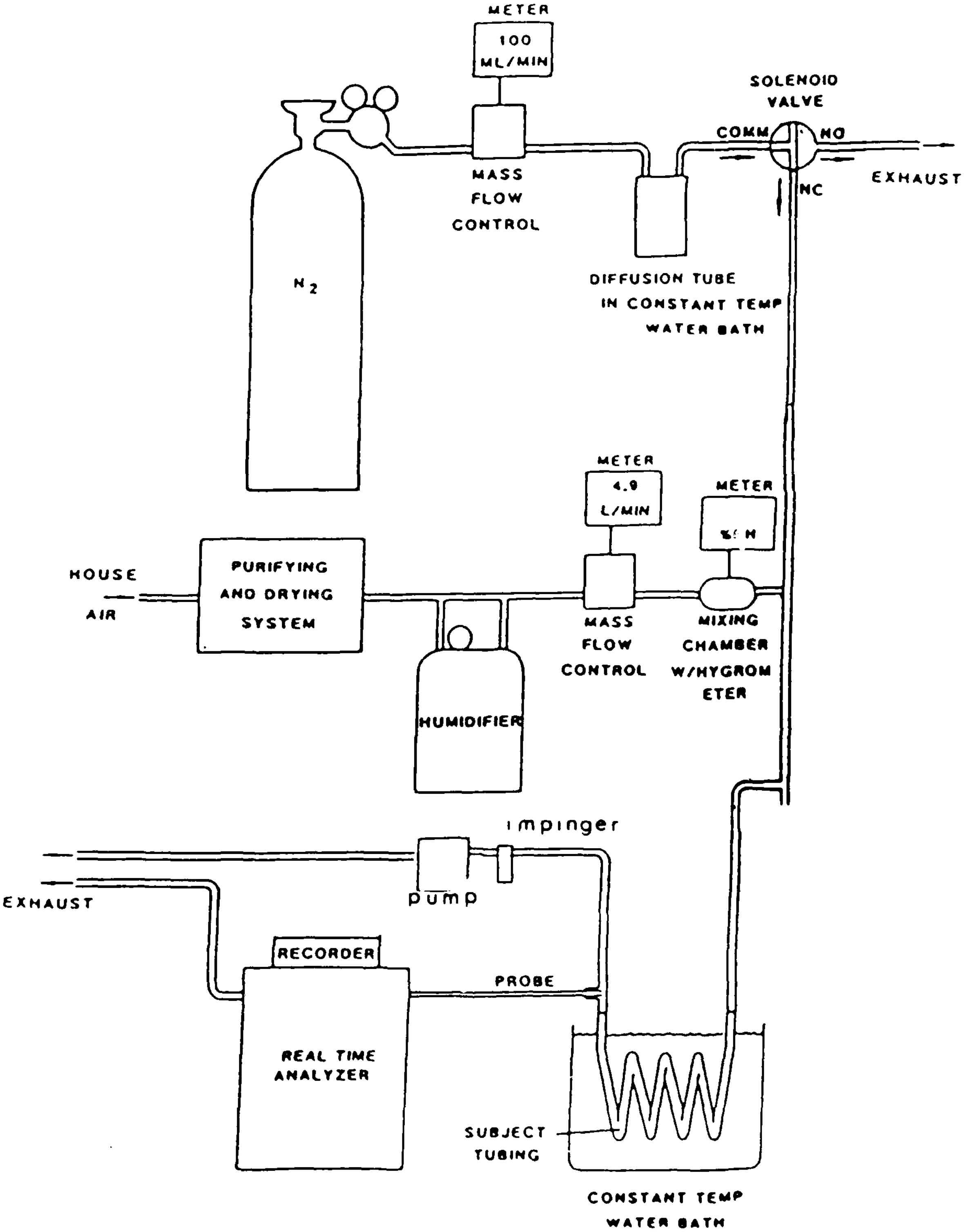

Figure 12. The modified apparatus for testing of material compatibility during experiments requiring "pulling" of the challenge gas.

Table 7. Effects of Pushing -vs- Pulling the 200 PPB MMH Air Stream Through 75 Feet of 1/4 Inch ID Tubing

Tubing Material	Flow Direction	Rate (L/Min)	50% (Min)	75% (Min)	90% (Min)	Max %	Min to Max
FEP	PUSH	5	1.25	3.25	12	97	35
FEP	PULL	3	2.5	7.5	--	88	33
HDPE	PUSH	5	2	4	13	94	29
HDPE	PULL	3	3	6	22	92	29
PFA	PUSH	5	4.5	10	30	94	66
PFA	PULL	3	6	12	--	87	31
POLYPROP	PUSH	5	1	2	9	97	36
POLYPROP	PULL	3	3	6.5	26	92	40
TFE	PUSH	5	2.5	6	22	96	45
TFE	PULL	3	4	18	77	90	77

Conditions: 20 C, 45% relative humidity.

which may explain the longer transport times observed. However the ranking of materials remained constant. Polypropylene and FEP yielded the best times and highest maximum percentages of MMH transported with HDPE a close third.

Phase 7 - Preconditioning of Tubing by Ambient Exposure

Two hundred foot samples of the most promising tubing materials were conditioned with ambient air. This procedure was accomplished by sampling 2.5 liters per minute of ambient air from the roof of the chemistry building at NRL. The sample coil and pump were sheltered, with the inlet of the tubing located in the open approximately 3 feet above the roof surface. Exposures were typically carried out for a period of one month. Following the conditioning, the tubings were evaluated for transport efficiency. The data collected is presented in Table 8. A direct comparison between tubings is not feasible since they did not all undergo the same conditioning. The polyethylene (polyeth) and the FEP were conditioned in the fall when high temperature and humidity prevailed. The Bev-a-line IV was not available until winter, therefore the ambient conditioning environments were different.

After extended conditioning with ambient air, samples showed a retardation in their ability to transport MMH. Polyethylene was affected to the greatest extent, so much so that the tubing essentially allowed no MMH through until it had been rinsed with methanol. The Bev-a-line IV was the only material to transport 100% after ambient exposure. Less than 50% was transported for the first 31 minutes, then a break-through seemed to occur, and 100% was reached in 34 minutes.

The results of the FEP pre- and post conditioning tests looked equivalent at the 50% and maximum percent transport times. The post exposure test took twice as long to reach 75% transport as the pre-exposure.

Table 8: The Effects Of Preconditioning Tubing With Ambient Air

Tubing Material	Length (feet)	Internal Diameter	50% (min)	75% (min)	90% (min)	MAX %	Min to Max %
polyeth	200	1/4"	--	--	--	--	--
^polyeth	200	1/4"	215	--	--	64	948
*polyeth	200	1/4"	10	54	--	86	474
FEP	193	1/4"	11	44	--	81	120
*FEP	193	1/4"	8.5	23	--	85	132
Bev	200	1/4"	31	31	31	100	34
*Bev	200	1/4"	5	7	21	100	51

*Data collected prior to ambient conditioning.

^Sample was washed with methanol following the ambient conditioning.

Conditions: 21 C and 45% RH. Pushing 200ppb MMH gas stream at 5 l/min.

CONCLUSIONS AND DISCUSSION

From the results obtained in the preliminary screening, metal tubings are not recommended. Many of the teflons and polymers proved to be acceptable candidates, including: Bev-a-line IV, FEP, HDPE, PFA, polyethylene, polypropylene, and TFE.

The clean Bev-a-line IV had the best transport properties. It was the only material tested to transport 100% at the increased lengths. Many of the above mentioned candidates had transport times and percentages which would be adequate for some applications. In addition the Bev-a-line IV exhibited the desired flexibility. Many of the other tubings showed a tendency to crimp.

The decision of which material to use must be made on an individual use basis. For shorter lengths some of the less expensive polymers will provide satisfactory performance. Some basic considerations to be made when selecting a tubing material are: length and flexibility needed, desired flow rate, cost, and whether location will allow access (for purposes of washing with methanol if needed). We have shown that the temperature and relative humidity of the environment to be sampled have essentially no effect on the selection. The environment of the areas the tubing will transverse must be taken into account and a material selected that can withstand the conditions.

The fate of the MMH which is not transported to the outlet of the tubing line has not been determined. The exhaust was monitored by the TECO analyzer which would not differentiate between MMH and NH_3, which is a known break-down product. An alternate instrument, the MDA 7100, which is not sensitive to NH_3, NO, or NO_2, was also used and gave a comparable MMH response. This suggests that break-down is not the reason for the loss.

In addition, the sampling line was checked for residual MMH by collecting and concentrating an acetone wash, and analyzing it by gas chromatography. No MMH was detected.

REFERENCES

1. J.A.E. Hannum, Recent Developments in the Toxicology of Propellant Hydrazines, Chemical Propulsion Information Agency, CPTR 82-15, June 1982.

2. Committee on Toxicology, "Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants", Vol. 5, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council, National Academy Press, Washington, DC 1985.

3. Edward C. Olson, Analytical Chemistry, 1960, 32(12), 1545.

4. J.R. Holtzclaw, S.L. Rose, and J.R. Wyatt, Analytical Chemistry, 1984, 56(14), 2952.